Reducing Corrosion Control Costs with Rapid-Cure Coatings

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NRL's Center for Corrosion Science and Engineering began work on the ONR Future Naval Capabilities (FNC) "Single Coat Program" in 2000. The goal was to reduce maintenance time and provide cost savings by introducing rapid-cure coatings technology to the fleet. Since program inception, NRL in conjunction with NAVSEA05M has successfully demonstrated the new rapid-cure coatings and advanced application process in more than 60 ship ballast tanks, comprising nearly 200,000 ft^2. There have been no reported in-service failures, the program has demonstrated costs savings of 25–30%, and the Navy will benefit greatly from a new class of qualified coatings. In addition to working with commercial partners, the Marine Coatings Section patented a new resin system and has formulated a new series of solvent-free, rapid-cure coatings designed specifically for shipboard use. These coatings, currently known as "novel resins," are cost-competitive with existing products and are of great interest commercially. They are scheduled for upcoming ship demonstration and final qualification.

INTRODUCTION

In 2000 the U.S. Navy instituted a seven-year program aimed at reducing corrosion control painting costs by incorporating rapid-cure coatings. The Single Coat Program, or rapid-cure coatings program, is sponsored by the Office of Naval Research (ONR) Undersea Weapons and Naval Materials Research Division. It represents the final step in a process of employing solvent-free coatings, instituted by NAVSEA's Materials Engineering Directorate (05M) as a means of reducing preservation costs while providing lifecycle extension to the Navy's ships. At the inception of this program, the use of rapid-cure coatings in the maritime industry was relatively unknown. The program has resulted in a nearly 30% reduction in cost and time with respect to corrosion control and maintenance painting. The Navy's rapid-cure program has also led to a worldwide interest in the use of rapid-cure coatings in commercial shipbuilding and repair for cost savings and lifecycle extension under the new International Maritime Organization (IMO) ballast tank painting protocol. Furthermore, the program has resulted in the development of a new class of coatings at the Naval Research Laboratory that are currently gaining widespread interest within the U.S. Navy and especially in the global commercial shipbuilding community.

Products

Products investigated and employed in the Single Coat Program include a broad spectrum of materials — epoxies, polyurethanes, polyureas, polyesters, and significant variations within these groups. The program focused mainly on two products: solvent-free, rapid-cure, epoxy-based coatings, and solvent-free, rapid-cure, polyurethane-based coatings.

Although no true definition of "rapid-cure" existed when the program began, any coating that exhibited a cure-to-handle time of three hours or less at an ambient temperature of 25 °C fit within the goals of the program.

Equipment

Successful and economical application of rapid-cure coatings depends on the use of specialized equipment called plural component equipment to supply and mix the base and hardener/catalyst components. The concept of plural component equipment is not new, but improvements for its use in the application of corrosion control coatings have been achieved through the efforts of this and other programs. Figure 1 shows typical plural component equipment configurations with the pump (or proportioner), supply lines, and mixing system for both static and impingement systems. The main difference between the two systems lies in where the coating components are mixed together — the faster the reaction time of the components, the closer to the spray gun the mixing is performed.

For materials with slow reaction speeds and/or minimal component solubility, a static mixer is employed. This configuration is typical for epoxy

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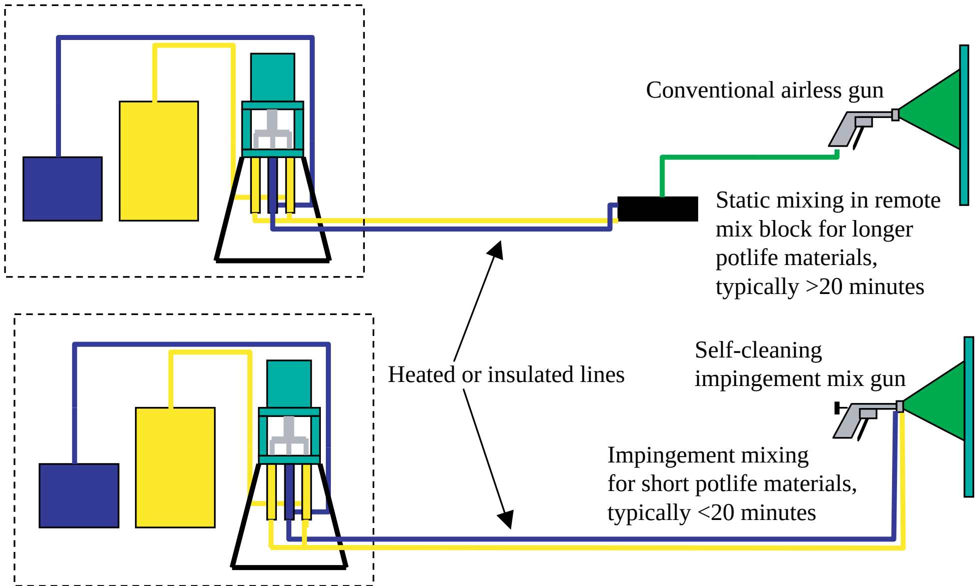


FIGURE 1
Basic attributes of static and impingement plural component systems.

coatings. The fast-cure epoxy coating components are fed via the proportioning pump in individual lines to a static mixer located on the pump itself or in a remote mix block typically located near the work area. From the mix block to the spray gun, the mixed coating is fed via a single line to a conventional airless spray gun.

For products with reaction times of less than one minute, the reaction speed is too fast to employ single-feed application of premixed material. For these products, an impingement mixing gun is employed, in which the components are kept separate until they reach the gun, where they mix and react. Each component must be 100% compatible and capable of thorough mixing at near instantaneous speeds. This is typical for polyurethane and polyurea products, which have extremely fast reaction speeds and very high component solubility. Because nearly all solvent-free polyurethanes have a working time of only a few seconds, that is, no "pot life," the components must be mixed and applied within a fraction of a second before film setting occurs — although the applied film may not cure hard for more than an hour.

Processes

It was immediately realized that the Single Coat Program would require a complete change in maintenance philosophy and process planning. Indeed, one of the goals of the program was to revamp the entire corrosion control painting process for ship's tanks and voids, and then to eventually transition this process to other areas within the ship maintenance painting community (i.e., exterior camouflage, internal quarters, and other coatings application process areas). The ultimate goal was to reduce the preservation time and associated costs. Figure 2 compares the conventional and rapid-cure processes and shows the estimated savings to be achieved from implementation of the latter.

DISCUSSION

Rapid-cure coatings represent a class of products whose chemistry is not unique or unknown. Rapid-cure epoxy adhesives, for example, have been employed for nearly 40 years in the highway industry to adhere roadway reflectors. A plural component dispenser supplies heated epoxy resin and hardener to the applicator holding the reflector. Once the mixed material is dispensed, the worker immediately places the reflector on the pavement, where the adhesive sets to become a near-permanent fixture on the roadway. Polyurethanes have also been used for many years, employed as spray-applied foams and insulation. Again, a plural component dispenser supplies the base and hardener through an impingement mixing gun to the work area.

What separates rapid-cure coatings from rapid-cure adhesives and foams is the basics of formulation. Whereas adhesives and foams are applied in large masses or thick films for adhesion and insulation, coatings are employed for corrosion control and aesthetics. Therefore, the coating formulations require specific properties of flow, leveling, color, and appearance, and for corrosion control coatings, a barrier and/or anti-corrosive performance. Many of the coatings initially evaluated in this program were simple adaptations of quick-setting adhesive formulations modified to

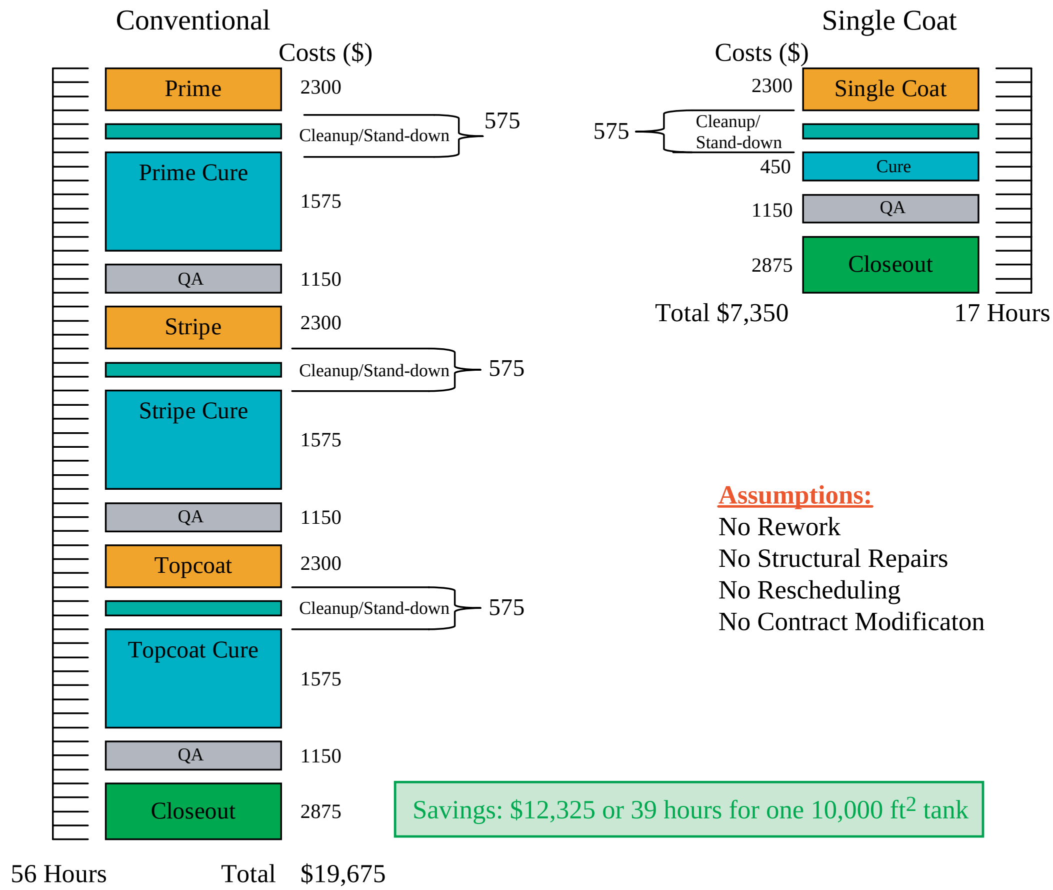


FIGURE 2
Original estimated cost savings using rapid-cure coatings on a 10,000 ft^2 tank.

perform as a coating. However, it became apparent that most, if not all, of these formulations lacked the attributes required for a corrosion control coating.

The Search for Rapid-Cure Coatings

Prior to and at the beginning of the Single Coat Program, the Marine Coatings Section at the Naval Research Laboratory identified commercial manufacturers of rapid-cure epoxy and polyurethane coatings to provide materials for testing. Emphasis was placed on securing a suitable commercial product to provide an early "proof of concept" to gain fleet support for the rapid-cure program. The rapid-cure epoxy systems available at the time were not suitable for shipboard tank applications — most were variations of existing solvent-based formulations filled with excessive catalyst, or were offensive-smelling polymercaptan-cured systems. Therefore, NRL chose commercial polyurethanes for initial testing and application. At the same time, because none of the available commercial products had all the attributes the Navy was looking for, NRL initiated development of its own materials and sought the use of alternative technologies, resulting in NRL's "novel resins," described below.

By mid-2000, the results of performance evaluation on two commercial polyurethane products were deemed favorable and NRL issued a public statement that these products would be demonstrated on a U.S. Navy ship within a short time. Epoxy manufacturers then responded with efforts to develop an improved, solvent-free, rapid-cure epoxy coating, and submitted samples for evaluation. Early performance was marginal, but epoxy manufacturers agreed they could make additional improvements.

Rapid-Cure Polyurethane Coatings

The formulation of polyurethanes, like all coatings, is part art and part science. The science portion relies on the chemistry of the polyol-isocyanate reaction to fulfill the basic properties of forming a solid material from two liquid components. The art is in understanding the behavior of the polyol and isocyanate components. Because of the reactivity of isocyanates with water, polyurethane coatings must be formulated from

what the industry calls "urethane grade" raw materials. All components, including pigments, fillers, and additives, must be free of water and any residual moisture. As little as 0.01% water can cause foaming, blistering, and improper curing of polyurethane coatings. Therefore the manufacture of polyurethane coatings takes place under dry or anhydrous conditions and typically in an inert gas environment. This makes the cost of polyurethane coatings slightly higher than that of other coatings whose resin components are more tolerant of water and moisture.

A basic polyurethane coating formulation consists of the pigmented polyol component that also contains the fillers and additives, and the unpigmented or "neat" isocyanate hardener. Although the isocyanate component can be pigmented, it is typically left unpigmented to ensure long storage stability. The coatings are formulated in an NCO/OH ratio, which refers to the ratio of isocyanate to polyol. Because one isocyanate reacts with one hydroxyl of the polyol, polyurethane coatings are formulated in an NCO/OH volumetric ratio as close to 1:1 as possible. Once the formulation has been established, the formulator makes a final adjustment to bring the NCO/OH ratio to between 1.01:1 and 1.05:1, resulting in a slight excess of 1 to 5% isocyanate. During application, a small percentage of NCO can react with airborne moisture and thus be rendered inactive, so a slight excess of isocyanate ensures availability for every OH group in the resin, and thus complete reaction of all the polyol.

Polyurethane coatings are not formulated to require a dwell or "induction" time. At the time of application, the isocyanate-polyol reaction proceeds to near completion almost immediately, its rate governed by several factors including ambient temperature, catalyst level, and isocyanate/polyol compatibility. It is important that solvent-free, rapid-curing polyurethane coatings are formulated with polyols that are mutually soluble with the isocyanate, as there is no solvent to assist in assuring component solubility. Indeed, the rapid-cure characteristics of the system prohibit the use of solvents, to avoid solvent entrapment in the cured film.

In the bulk film, the isocyanate-polyol reaction results in nearly 100% polyurethane; however, at the surface, the reaction forms a mix of polyurethane and polyurea. The polyurea reaction is a result of unreacted isocyanate at the surface reacting with airborne moisture rather than with the polyol. As the isocyanate reacts with moisture, it is converted to an amine which in turn reacts extremely rapidly with any available isocyanate. The polyurea reaction at the surface is controlled by the amount of moisture in the air: the higher the relative humidity, the more pronounced the reaction. This phenomenon is less pronounced with solvent-borne polyurethanes, as the escaping solvent shields the coating surface from moisture, thus preserving a more uniform urethane structure. The polyurea reaction in a solvent-free polyurethane coating formulation is important for industrial coatings application because it has a dramatic effect on the overcoat window of the applied system. Because the polyurea "skin" is highly solvent-resistant (not to be confused with commercial polyurea coatings, which do not have high chemical resistance), it presents a problem with adhesion of the next coat. Therefore each coat of a solvent-free polyurethane should be performed in rapid succession to minimize contamination of the base coat and maximize adhesion. Because a solvent-free polyurethane can be catalyzed to react quickly, the rapid application of successive coats is possible; this is one of the primary benefits of these systems.

RESULTS

Demonstrations of Commercial Products

Polyurethanes: In May 2002, the first rapid-cure demonstration took place when a simply configured 3,000 ft^2 seawater ballast tank was painted using a solvent-free, rapid-cure polyurethane; see Fig. 3. Figure 4 shows the same tank after six months of service. Despite the anticipation of massive failure and unforeseen difficulties, the application was a complete success. The operator had never applied a rapid-cure polyurethane, but the application was simple and straightforward; some initial difficulties were quickly resolved. This first-ever application of a solvent-free, rapid-cure polyurethane to a U.S. Navy ship represented the first step in perhaps the most significant change to affect shipbuilding in nearly 50 years. For the first time, a tank was painted from start to finish with the complete coating system in *one day*.

The first application came with a hefty price tag of nearly \$46/ft^2 (\$28/ft^2 for painting cost only). The high cost was due to the lack of familiarity with the new system; it included a "safety net" consisting of provisions to reblast the tank and apply a conventional coating should the experimental system fail or suffer from improper application. This risk aversion concept was put into practice several more times before it became apparent that application failures were not going to occur and that the use of rapid-cure coatings was meeting the program goals of saving time and money.

In early 2003, the second application of the same solvent-free, rapid-cure polyurethane took place in a seawater ballast tank of higher complexity and comprising approximately 2,500 ft^2. Using the lessons learned from the first application, the cost was reduced to \$32/ft^2 (\$18/ft^2 for painting only). The process took one day for application and a second day for touchup

FIGURE 3
Results of the first solvent-free, rapid-cure polyurethane application in a seawater ballast tank.

FIGURE 4
Results of the first polyurethane system application after six months in service.

in areas not accessible by spray application. In late 2003, a void space of similar area and increased complexity was coated with the same system at a cost of \$28/ft^2 (\$14/ft^2 for painting only). The application again took one day for full application and one day for touchup.

In early 2004, a second polyurethane product was demonstrated in a highly confined drinking (potable) water tank and simultaneously in a complex seawater ballast tank for a combined cost of \$20/ft^2 (\$6/ft^2 for painting only). Both tanks were completed in a two day period. Figure 5 shows the polyurethane coating performance in the drinking water tank after two years of service. The original solvent-based epoxy system had barely lasted one year before failing.

Epoxies: In June 2003, after performance evaluation at NRL's Key West Marine Coatings Test Facility, the first rapid-cure epoxy coating made its debut in a U.S. Navy ship. Figure 6 shows the final application of a rapid-cure epoxy coating as applied to a 19,000 ft^2 seawater ballast tank over a period of two days. The cost for application was less than \$21/ft^2 (\$7/ft^2 for painting only). The primary contributor to this significant cost savings was the fast-curing performance of the coating, combined with the large surface area of the tank. The tank was large enough that as one painting crew was finishing application of the first coat, a second crew entered and began applying the stripe coat. A stripe coat is an additional application of product to corners, welds, edges, and other locations, performed as a safety precaution to ensure complete substrate coverage. On the second day, the topcoat was applied and the job was completed. This demonstration represented a significant achievement in the use of epoxy coatings for corrosion control in that it was the first time that two coats of an epoxy system (prime and stripe) were applied to a tank in one day. This would not have been possible with a conventional epoxy coating.

NRL's "Novel Resins"

At the same time that commercial products were being advanced, NRL initiated in-house development of new materials to support the rapid-cure program. Early in the Single Coat Program, it became apparent that there were notable deficiencies with the commercially available polyurethane and epoxy coatings. Although the coatings demonstrated a majority of

FIGURE 5
Performance results of solvent-free, rapid-cure polyurethane in a drinking water tank after two years of service. The tank is not equipped with sacrificial or induced cathodic protection; corrosion control is afforded only by the coating. The rust staining is from TLI mounting brackets only.

FIGURE 6
Completed application of fast-cure epoxy in a 19,000 ft^2 tank.

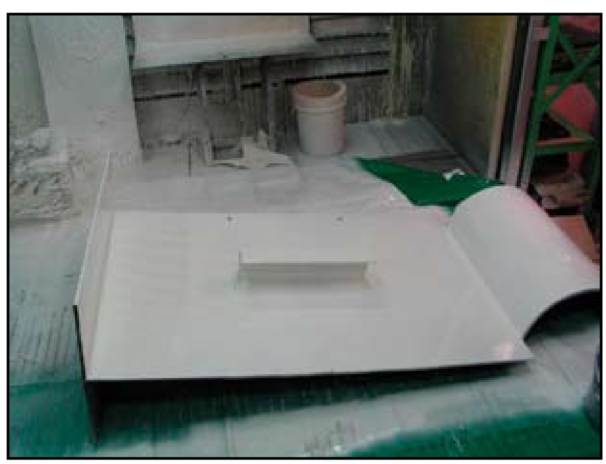
the required performance and handling attributes, their overall suitability and long-term performance were not clearly established. Therefore, researchers at NRL devised a series of radically new solvent-free polyol materials for rapid-cure polyurethanes. These "novel resins" are based on raw materials commercially available to any coatings manufacturer; furthermore, the synthesis reactions can be performed in any well equipped coatings manufacturing facility. For example, any facility equipped to manufacture its own alkyd or polyester resins has sufficient capital resources to manufacture the NRL resin systems.

The novel resins are a series of amino polyols that when fully synthesized possess the chemical resistance and corrosion control attributes of an epoxy coating along with the rapid-cure characteristics of a polyurethane. The term "amino polyol" is used because the resins are synthesized from two processes: the reaction of alkanol amines with polyfunctional epoxy materials, or the reaction of polyamines with monofunctional epoxide-containing materials — the perfect marriage of two distinct material classes into one universal product offering the most positive attributes of each.

Three main working formulations and about a dozen intermediates have been developed, each with specific performance attributes. The three main products are a low viscosity, low molecular weight material for use alone or as a reactive diluent, a medium viscosity material for light to medium duty coatings, and a higher viscosity version for heavy duty harsh chemical applications. To date, the most sought-after version is the light to medium duty medium viscosity version, as it offers the most epoxy-like handling characteristics with the most attractive rapid-cure polyurethane traits. At present, the product is being licensed and manufactured for commercial use. The system has also been the subject of a detailed and highly publicized productivity study in a commercial shipyard in the Far East; it has been deemed a viable candidate for changing the commercial shipbuilding industry to allow a nearly 40% increase in painting productivity resulting in 20% overall savings to the yard while also meeting the new IMO requirements for a 15-year coating system for seawater ballast tanks on commercial ships.

Figure 7 shows the results of a test application at the commercial shipyard in the Far East using the NRL system as a high-build two-coat product. The entire

FIGURE 7
Results of NRL novel resin application to a productivity study test piece.



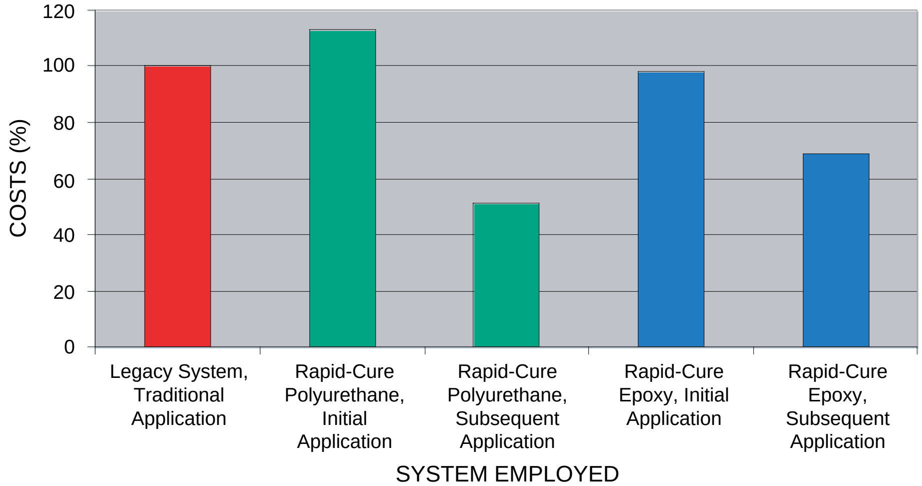


FIGURE 8
Application costs of rapid-cure polyurethane and epoxy systems relative to legacy system.

part was coated in less than 15 minutes, with the full system applied in two coats. The part was cured to handle 20 minutes after application of the second coat. A comparative application using a traditional solvent-based, three-coat epoxy took three days, as each coat had to cure eight hours before the next coat could be applied.

CONCLUSIONS

The rapid-cure program has been overwhelmingly successful and has gained significant interest within the fleet. Rapid-cure coatings are now on the Navy's Qualified Products List (QPL) and have also been adopted for corrosion control on submarines.

Figure 8 compares the costs of the polyurethane and epoxy technologies based on first-time (demonstration) application and follow-on (standard production) applications. In each case, reduction in job cost was directly related to the fast cure times. Faster curing lowers the risks of production delays and premature damage.

This program has clearly demonstrated that the application of rapid-cure coatings results in significant cost reduction under the maintenance and repair processes that are prevalent in the U.S. Navy. The cost savings realized under repair processes can be further realized under new building in the military and commercial ship construction sectors.

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